(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
25 January 2001 (25.01.2001)

PCT

(10) International Publication Number
WO 01/06053 A1

(51) International Patent Classification[7]: D06L 1/00, 1/02, B05D 1/00, C11D 1/82, 3/39, 3/43

(21) International Application Number: PCT/US00/19790

(22) International Filing Date: 20 July 2000 (20.07.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/144,624	20 July 1999 (20.07.1999)	US
09/621,314	20 July 2000 (20.07.2000)	US

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(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*
— *Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/06053 A1

(54) Title: PRE-TREATMENT METHODS AND COMPOSITIONS FOR CARBON DIOXIDE DRY CLEANING

(57) Abstract: A method for dry-cleaning articles such as fabrics and clothing in carbon dioxide. The article includes a stained portion or region, which is pretreated with a pretreatment composition prior to initiating the cleaning cycle. The pretreatment step is followed by contacting the pretreated article to be cleaned with a liquid dry cleaning composition for a time sufficient to clean the article. The liquid dry-cleaning composition comprises a mixture of carbon dioxide, a surfactant, and an organic co-solvent. After the contacting step, the article is separated from the liquid dry cleaning composition. The pretreatment composition, in a preferred embodiment, comprises at least one of (a) a surfactant; (b) d-limonene, and (c) a C12-C15 alkane co-solvent. Preferably the pretreatment composition comprises at least two, and in some particularly preferred embodiments, the pretreatment composition comprises all three, of the aforesaid ingredients.

PRE-TREATMENT METHODS AND COMPOSITIONS FOR CARBON DIOXIDE DRY CLEANING

Related Applications

This application claims priority from United States Provisional application Serial No. 60/144,624, filed July 20, 1999, the disclosure of which is incorporated by reference herein in its entirety.

Field of the Invention

The present invention relates to methods and compositions for carrying out the dry-cleaning of fabrics (*e.g.*, garments) in liquid carbon dioxide.

Background of the Invention

Commercial dry cleaning systems currently employ potentially toxic and environmentally harmful halocarbon solvents, such as perchloroethylene. Carbon dioxide has been proposed as an alternative to such systems in U.S. Patent No. 4,012, 194 to Maffei.

German Patent Application DE3904514 A1 of Schollmeyer, published August 23, 1990, describes a cleaning system combining various conventional anionic or nonionic surface active agents with supercritical CO_2. The system described therein appears to combine the detergency mechanism of conventional surface active agents with the solvent power of supercritical fluid carbon dioxide. A carbon dioxide dry cleaning system effective for liquid carbon dioxide is not provided.

U.S. Patent No. 5,683,473 to Jureller et al. (see also 5,683,977 to Jureller et al.) describes a dry cleaning system utilizing carbon dioxide in liquid form in

combination with surfactants that contain a functional moiety that is CO_2-philic, which surfactants are not conventionally used for detergent cleaning. Since there are numerous advantages to employing conventional surfactants (*e.g.*, cost, ready availability, established regulatory approval, established toxicology, etc), it would be extremely desirable to have a dry cleaning system for liquid carbon dioxide that employs conventional surfactants that do not contain a CO_2-philic group.

U.S. Patent No. 5,858,022 to Romack et al. describes dry methods and compositions for dry cleaning in liquid carbon dioxide formulations in which a conventional surfactant (*i.e.*, one that does not contain a CO_2-philic group) is used in combination with an organic co-solvent. The conventional surfactant is soluble in the organic co-solvent. Ingredients such as bleaches, whiteners, softeners, sizing, starching, enzymes, hydrogen peroxide or a source of hydrogen peroxide, are described at column 3 lines 39-43, but recommendations for the structure or composition of ingredients that are particularly advantageous in carbon dioxide cleaning formulations, as opposed to functional statements thereof, are not provided. Accordingly, there is a continued need for additives or ingredients that can be advantageously employed with carbon dioxide cleaning formulations.

Summary of the Invention

A method for dry-cleaning garments or fabrics in carbon dioxide, said garment or fabric including a stained portion comprises pre-treating the stained portion of a garment or fabric article to be cleaned with a liquid pretreatment composition, said composition preferably containing a pretreatment surfactant. The pretreatment step is followed by the steps of contacting the article with a liquid dry cleaning composition for a time sufficient to clean the article, said liquid dry-cleaning composition comprising a mixture of carbon dioxide and a cleaning surfactant; and then separating the article from the liquid dry cleaning composition.

In one embodiment, the pretreatment surfactant is one which does not contain a CO_2-philic group. In another embodiment, the pretreatment surfactant is one which does contain a CO_2-philic group (*e.g.*, a fluoropolymer or a fluorine-containing segment such as a fluoroacrylate polymer, or a siloxane polymer or siloxane containing segment), which CO_2-philic group is in turn coupled to a hydrophilic or

lipophilic group. When present, the pretreatment surfactant (either type) is preferably included in an amount of from 0.05, 1, 2, or 3 percent to 5 or 10 percent by weight.

Without wishing to be bound to any particular theory of the invention, it is believed that surfactants that do not contain a CO_2-philic group remain localized in the area to which they are applied to a greater extent during the cleaning cycle in the presence of the carbon dioxide cleaning solution and facilitate holding water to the stained area, thus facilitating cleaning of the stained area during the cleaning cycle.

When the surfactant comprises a CO_2-philic group coupled to a lipophilic segment, the pretreatment composition is particularly useful for grease, oily stains and the like (*e.g.*, hydrophobic stains). When the surfactant comprises a CO_2-philic group coupled to a hydrophilic segment, the pretreatment composition is particularly useful for protein and tanin-type stains and the like (*e.g.*, hydrophilic stains).

In another embodiment of the invention, the pretreatment surfactant is a poly(ether-carbonate) copolymer. Again, when present, the pretreatment surfactant is preferably included in an amount of from 1, 2, or 3 percent to 5 or 10 percent by weight of the total formulation (the surfactant may be one or a combination of surfactants as described above).

Preferably, the cleaning composition comprises (or further comprises, in addition to the surfactants noted above) an organic co-solvent. Particularly preferred organic co-solvents are C12-C15 alkane co-solvents. When present, such organic co-solvents are preferably included in an amount of from 2, 30 or 40 percent to 70, 80 or 90 percent by volume.

In another embodiment, the pretreatment composition contains d-limonene, either alone or, more preferably, in combination with an organic co-solvent (particularly a C12-15 alkane co-solvent as above), and/or a surfactant as noted above. When present, the d-limonene is included in the pretreatment composition in an amount of from 5 or 10 percent to 30, 40 or 50 percent, by volume.

The balance of the pretreatment compositions described above may comprise water.

A particularly preferred pretreatment composition includes both an organic co-solvent as described above and d-limonene as described above. Such a composition optionally but preferably also includes a surfactant or surfactants as described above.

Detailed Description of the Invention

The term "pretreatment" as used herein refers to contacting a pretreatment composition, typically a liquid, to a stained portion or particular region of an article to be cleaned so that the pretreatment composition is deposited on that portion or region in an amount effective to enhance subsequent cleaning of the article, and then continuing or initiating further dry cleaning of that article with the pretreatment composition deposited upon the article to be cleaned.

The term "clean" as used herein refers to any removal of soil, dirt, grime, or other unwanted material, whether partial or complete. The invention may be used to clean nonpolar stains (*i.e.*, those which are at least partially made by nonpolar organic compounds such as oily soils, sebum and the like), polar stains (*i.e.*, hydrophilic stains such as grape juice, coffee and tea stains), compound hydrophobic stains (*i.e.*, stains from materials such as lipstick and candle wax), and particular soils (*i.e.*, soils containing insoluble solid components such as silicates, carbon black, etc.).

Articles that can be pretreated and cleaned by the methods of the present invention are, in general, garments and fabrics (including woven and non-woven) formed from materials such as cotton, wool, silk, leather, rayon, polyester, acetate, fiberglass, furs, etc., formed into items such as clothing, work gloves, rags, leather goods (*e.g.*, handbags and brief cases), etc.

The present invention may be carried out in any suitable carbon-dioxide based dry cleaning system, such as those described in U.S. Patents Nos. 5,858,022 to Romack et al. or 5,683,473 to Jureller et al., the disclosures of which are incorporated by reference herein in their entirety.

1. Cleaning compositions and processes.

Liquid dry-cleaning compositions useful for carrying out the present invention typically include water. The source of the water is not critical in all applications. The water may be added to the liquid solution before the articles to be cleaned are deposited therein, may be atmospheric water, may be the water carried by the garments, etc.

In one embodiment of the invention, better particulate cleaning may be obtained in the absence of water added to the dry-cleaning composition. There is inherently water present on or in the garments or articles to be cleaned as they are

placed in the cleaning vessel. This water serves in part to adhere particulate soil to the articles to be cleaned. As the water is removed from the garments into the cleaning composition during the cleaning process, the removal of water from the article to be cleaned facilitates the removal of particulates from the articles to be cleaned. Thus, decreasing the amount of water originally in the cleaning system can serve to facilitate the cleaning of particulate soil from the articles to be cleaned by the action of the water inherently carried by the article to be cleaned.

Liquid dry-cleaning compositions useful for carrying out the present invention typically comprise:

(a) from zero (0), 0.02, 0.05 or 0.1 to 5 or 10 percent (more preferably from .1 to 4 percent) water;

(b) carbon dioxide (to balance; typically at least 30 percent);

(c) surfactant (preferably from 0.1 or .5 percent to 5 or 10 percent total, which may be comprised of one or more different surfactants); and

(d) from 0.1 to 50 percent (more preferably 1, 2 or 4 percent to 30 percent) of an organic co-solvent.

Percentages herein are expressed as percentages by weight unless otherwise indicated.

The composition is provided in liquid form at ambient, or room, temperature, which will generally be between zero and 50° Centigrade. The composition is held at a pressure that maintains it in liquid form within the specified temperature range. The cleaning step is preferably carried out with the composition at ambient temperature. For the purposes of the invention, the pretreatment composition may be a heterogeneous or homogeneous composition.

The organic co-solvent is, in general, a hydrocarbon co-solvent. Typically the co-solvent is an alkane co-solvent, with C_{10} to C_{20} linear, branched, and cyclic alkanes, and mixtures thereof (preferably saturated) currently preferred. The organic co-solvent preferably has a flash point above 140°F, and more preferably has a flash point above 170°F. The organic co-solvent may be a mixture of compounds, such as mixtures of alkanes as given above, or mixtures of one or more alkanes. Additional compounds such as one or more alcohols (*e.g.*, from 0 or 0.1 to 5% of a C1 to C15 alcohol (including diols, triols, etc.)) different from the organic co-solvent may be included with the organic co-solvent.

Examples of suitable co-solvents include, but are not limited to, aliphatic and aromatic hydrocarbons, and esters and ethers thereof, particularly mono and di-esters and ethers (*e.g.*, EXXON ISOPAR L, ISOPAR M, ISOPAR V, EXXON EXXSOL, EXXON DF 2000, CONDEA VISTA LPA-170N, CONDEA VISTA LPA-210, cyclohexanone, and dimethyl succinate), alkyl and dialkyl carbonates (*e.g.*, dimethyl carbonate, dibutyl carbonate, di-t-butyl dicarbonate, ethylene carbonate, and propylene carbonate), alkylene and polyalkylene glycols, and ethers and esters thereof (*e.g.*, ethylene glycol-n-butyl ether, diethylene glycol-n-butyl ethers, propylene glycol methyl ether, dipropylene glycol methyl ether, tripropylene glycol methyl ether, and dipropylene glycol methyl ether acetate), lactones (*e.g.*, (gamma)butyrolactone, (epsilon)caprolactone, and (delta) dodecanolactone), alcohols and diols (*e.g.*, 2-propanol, 2-methyl-2-propanol, 2-methoxy-2-propanol, 1-octanol, 2-ethyl hexanol, cyclopentanol, 1,3-propanediol, 2,3-butanediol, 2-methyl-2,4-pentanediol) and polydimethylsiloxanes (*e.g.*, decamethyltetrasiloxane, decamethylpentasiloxane, and hexamethyldisloxane), etc.

Any surfactant can be used to carry out the present invention, including both surfactants that contain a CO_2-philic group (such as described in PCT Application WO96/27704) linked to a CO_2-phobic group (*e.g.*, a lipophilic group or hydrophobic group) and (more preferably) surfactants that do not contain a CO_2-philic group (*i.e.*, surfactants that comprise a hydrophilic group linked to a hydrophobic (typically lipophilic) group). A single surfactant may be used, or a combination of surfactants may be used.

Numerous surfactants are known to those skilled in the art. *See, e.g.*, McCutcheon's Volume 1: Emulsifiers & Detergents (1995 North American Edition) (MC Publishing Co., 175 Rock Road, Glen Rock, NJ 07452). Examples of the major surfactant types that can be used to carry out the present invention include the: alcohols, alkanolamides, alkanolamines, alkylaryl sulfonates, alkylaryl sulfonic acids, alkylbenzenes, amine acetates, amine oxides, amines, sulfonated amines and amides, betaine derivatives, block polymers, carboxylated alcohol or alkylphenol ethoxylates, carboxylic acids and fatty acids, diphenyl sulfonate derivatives, ethoxylated alcohols, ethoxylated alkylphenols, ethoxylated amines and/or amides, ethoxylated fatty acids, ethoxylated fatty esters and oils, fatty esters, fluorocarbon-based surfactants, glycerol esters, glycol esters, heterocyclic-type products, imidazolines and imidazoline

derivatives, isethionates, lanolin-based derivatives, lecithin and lecithin derivatives, lignin and lignin derivatives, maleic or succinic anhydrides, methyl esters, monoglycerides and derivatives, olefin sulfonates, phosphate esters, phosphorous organic derivatives, polyethylene glycols, polymeric (polysaccharides, acrylic acid, and acrylamide) surfactants, propoxylated and ethoxylated fatty acids alcohols or alkyl phenols, protein-based surfactants, quaternary surfactants, sarcosine derivatives, silicone-based surfactants, soaps, sorbitan derivatives, sucrose and glucose esters and derivatives, sulfates and sulfonates of oils and fatty acids, sulfates and sulfonates, ethoxylated alkylphenols, sulfates of alcohols, sulfates of ethoxylated alcohols, sulfates of fatty esters, sulfonates of benzene, cumene, toluene and xylene, sulfonates of condensed naphthalenes, sulfonates of dodecyl and tridecylbenzenes, sulfonates of naphthalene and alkyl naphthalene, sulfonates of petroleum, sulfosuccinamates, sulfosuccinates and derivatives, taurates, thio and mercapto derivatives, tridecyl and dodecyl benzene sulfonic acids, etc.

Additional examples of surfactants that can be used to carry out the present invention include alcohol and alkylphenol polyalkyl ethers (*e.g.*, TERGITOL 15-S-3™ secondary alcohol ethoxylate, TRITON X-207™ dinonylphenol ethoxylate, NEODOL 91-2.5™ primary alcohol ethoxylate, RHODASURF BC-410™ isotridecyl alcohol ethoxylate, RHODASURF DA-630™ tridecyl alcohol ethoxylate) alkylaryl carbonates, including salts and derivatives thereof (*e.g.*, acetic acid, MARLOWET 4530™ dialkylphenol polyethylene glycol acetic acid, MARLOWET 1072™ alkyl polyethylene glycol ether acetic acid), alkoxylated fatty acids (*e.g.*, NOPALCOL 1-TW™ diethylene glycol monotallowate, TRYDET 2600™ polyoxyethylene (8) monostearate), alkylene oxide block copolymers (*e.g.*, PLURONIC™ and TETRONIC™ products), acetylenic alcohols and diols (*e.g.*, SURFYNOL™ and DYNOL™ products), mono- and di-esters of sulfosuccinic acid (*e.g.*, AEROSOL OT™ sodium dioctyl sulfosuccinate, AEROSOL IB-45™ sodium diisobutyl sulfosuccinate, MACKANATE DC-50™ dimethicone copolyol disodium sulfosuccinate, SOLE TERGE-8™ oleic acid isopropanolamide monoester of sodium sulfosuccinate), sulfosuccinamic acid and esters thereof (*e.g.* AEROSOL 18™ disodium-N-octadecyl sulfosucciniamate, AEROSOL 22™ tetrasodium N-(1,2-dicarboxyethyl)-N octadecyl sulfosuccinamate) sorbitan esters including derivatives thereof (*e.g.*, SPAN 80™ sorbitan monoleate, ALKAMULS 400-DO™ sorbitan

dioleate, ALKAMULS STO™ sorbitan trioleate, TWEEN 81™ polyoxyethylene (5) sorbitan monoleate, TWEEN 21™ polyoxyethylene (4) sorbitan monolaurate), isothionates including derivatives thereof (*e.g.*, GEROPON AC-270™ sodium cocoyl isothionate), polymeric alkylaryl compounds and lignins, including derivatives thereof (*e.g.*, LIGNOSITE 50™ calcium lignosulfonate), alkylaryl sulfonic acids and salts thereof (*e.g.*, CALIMULSE EM-99™ branched dodecylbenzene sulfonic acid, WITCONATE C-50H™ sodium dodecylbenzene sulfonate, WITCONATE P10-59™ amine salt of dodecylbenzene sulfonate), sulfonated amines and amides (*e.g.*, CALIMULSE PRS™ isopropylamine sulfonate), Betaine and sultaine derivatives, and salts thereof (*e.g.*, lauryl sulfobetaine, dodecyldimethyl(3-sulfopropyl)ammonium hydroxide, FOAMTAIN CAB-A™ cocamidopropyl betaine ammonium salt, FOAMTAINE SCAB™ cocamidopropyl hydroxy sultaine), *e.g.*, imidazolines including derivatives thereof (*e.g.*, MONOAZOLINE O™ substituted imidazoline of oleic acid, MONOAZOLINE T™ substituted imidazoline of Tall Oil), oxazolines including derivatives thereof (*e.g.*, ALKATERGE E™ oxazoline derivative, ALKATERGE T-IV™ ethoxylated oxazoline derivative), carboxylated alcohol or alkylphenol ethoxylates including derivatives thereof (*e.g.*, MARLOSOL OL7™ oleic acid polyglycol ester), diphenyl sulfonates including derivatives thereof (*e.g.*, DOWFAX™ detergent diphenyl oxide disulfonate, DOWFAX™ dry detergent: sodium n-hexadecyl diphenyl oxide disulfonate, DOWFAX™ Dry hydrotrope: sodium hexyl diphenyloxide disulfonate) fluorinated surfactants (*e.g.*, FLUORAD FC-120™ ammonium perfluoroalkyl sulfonate, FLUORAD FC-135™ fluoroalkyl quaternary ammonium iodides, FLUORAD FC-143™ ammonium perfluoroalkyl carboxylates), lecithins including lecithin derivatives (*e.g.*, ALCOLEC BS™ soy phosphatides), phosphate esters (*e.g.*, ACTRAFOS SA-216™ aliphatic phosphate ester, ACTRAFOS 110™ phosphate ester of complex aliphatic hydroxyl compound, CHEMPHOS TC-310™ aromatic phosphate ester, CALGENE PE-112N™ phosphated mono- and diglycerides), sulfates and sulfonates of fatty acids (*e.g.*, ACTRASOL PSR™ sulfated castor oil, ACTRASOL SR75™ sulfated oleic acid), sulfates of alcohols (*e.g.*, DUPONOL C™ sodium lauryl sulfate, CARSONOL SHS™ sodium 2-ethyl-1-hexyl sulfate, CALFOAM TLS-40™ triethanolamine lauryl sulfate), sulfates of ethoxylated alcohols (*e.g.*, CALFOAM ES-301™ sodium lauryl ether sulfate), amines, including salts and derivatives thereof (*e.g.*,

Tris(hydroxymethyl)aminomethane, ARMEEN™ primary alkylamines, ARMAC HT™ acetic acid salt of N-alkyl amines) amide sulfonates (*e.g.*, GEROPON TC-42™ sodium N-coconut acid-N-methyl taurate, GEROPON TC 270™ sodium cocomethyl tauride), quaternary amines, including salts and derivatives thereof (*e.g.*, ACCOSOFT 750™ methyl bis (soya amidoethyl)-N-polyethoxyethanol quaternary ammonium methyl sulfate, ARQUAD™ N-alkyl trimethyl ammonium chloride, ABIL QUAT 3272™ diquaternary polydimethylsiloxane), amine oxides (*e.g.*, AMMONYX CO™ cetyl dimethylamine oxide, AMMONYX SO™ stearamine oxide), esters of glycerol, sucrose, glucose, sarcosine and related sugars and hydrocarbons including their derivatives (*e.g.*, GLUCATE DO™ methyl glucoside dioleate, GLICEPOL 180™ glycerol oleate, HAMPOSYL AL-30™ ammonium lauroyl sarcosinate, HAMPOSYL M™ N-myristoyl sarcosine, CALGENE CC™ propylene glycol dicaprylate/dicaprate), polysaccharides including derivatives thereof (*e.g.*, GLUCOPON 225 DK™ alkyl polysaccharide ether), protein surfactants (*e.g.*, AMITER LGS-2™ dioxyethylene stearyl ether diester of N-lauroyl-L-glutamic acid, AMISOFT CA™ cocoyl glutamic acid, AMISOFT CS 11™ sodium cocoyl glutamate, MAYTEIN KTS™ sodium/TEA lauryl hydrolyzed keratin, MAYPON 4C™ potassium cocoyl hydrolyzed collagen), and including thio and mercapto derivatives of the foregoing (*e.g.*, ALCODET™ polyoxyethylene thioether, BURCO TME™ ethoxylated dodecyl mercaptan), etc. Thus the present invention may be carried out using conventional surfactants, including but not limited to the anionic or nonionic alkylbenzene sulfonates, ethoxylated alkylphenols and ethoxylated fatty alcohols described in Schollmeyer German Patent Application DE 39 04514 A1.

Surfactants that contain a CO_2-philic group are described are known in the art and described in, for example, J. DeSimone et al., *Science* **265**, 356 (1994), U.S. Patent No. 5,312,882 to DeSimone et al., U.S. Patent No. 5,683,473 to Jureller et al. and U.S. Patent No. 5,683,977 to Jureller et al.

As will be apparent to those skilled in the art, numerous additional ingredients can be included in the dry-cleaning composition, including detergents, bleaches, whiteners, softeners, sizing, starches, enzymes, hydrogen peroxide or a source of hydrogen peroxide, fragrances, etc.

In practice, in a preferred embodiment of the invention, an article to be cleaned and a liquid dry cleaning composition as given above are combined in a

closed drum. The liquid dry cleaning composition is preferably provided in an amount so that the closed drum contains both a liquid phase and a vapor phase (that is, so that the drum is not completely filled with the article and the liquid composition). The article is then agitated in the drum, preferably so that the article contacts both the liquid dry cleaning composition and the vapor phase, with the agitation carried out for a time sufficient to clean the fabric. The cleaned article is then removed from the drum. The article may optionally be rinsed (for example, by removing the composition from the drum, adding a rinse solution such as liquid CO_2 (with or without additional ingredients such as water, co-solvent, etc.) to the drum, agitating the article in the rinse solution, removing the rinse solution, and repeating as desired), after the agitating step and before it is removed from the drum. The dry cleaning compositions and the rinse solutions may be removed by any suitable means, including both draining and venting.

Any suitable cleaning apparatus may be employed, including both horizontal drum and vertical drum apparatus. When the drum is a horizontal drum, the agitating step is carried out by simply rotating the drum. When the drum is a vertical drum it typically has an agitator positioned therein, and the agitating step is carried out by moving (*e.g.*, rotating or oscillating) the agitator within the drum. A vapor phase may be provided by imparting sufficient shear forces within the drum to produce cavitation in the liquid dry-cleaning composition. Finally, in an alternate embodiment of the invention, agitation may be imparted by means of jet agitation as described in U.S. Patent No. 5,467,492 to Chao et al., the disclosure of which is incorporated herein by reference. A particularly preferred apparatus is described in U.S. Patent No. 6,049,331 to McClain et al. As noted above, the liquid dry cleaning composition is preferably an ambient temperature composition, and the agitating step is preferably carried out at ambient temperature, without the need for associating a heating element with the cleaning apparatus.

2. Pretreatment compositions and processes.

In one embodiment, a liquid pre-treatment composition useful for carrying out the present invention typically comprises:

(a) water (to balance; typically at least 30, 40 or 50 percent);

(b) a surfactant (preferably from 0.1 or .5 percent to 5 or 10 percent total, which may be comprised of one or more different surfactants); and

(c) from zero (0) or 1 to 40 percent (more preferably 2 or 4 percent to 30 percent) of an organic co-solvent)(or in another preferred embodiment from 30 or 40 to 80 percent by volume), with C12-C15 alkane cosolvents particularly preferred.

The surfactant and any organic co-solvent may be any of those described above in connection with the cleaning formulations, or the surfactant may be a poly(ether-carbonate) copolymer as described below.

In one embodiment, the surfactant contains a CO_2-philic group as noted above. In another embodiment. the surfactant does not contain a CO_2-philic group.

Surfactants that do not contain a CO_2-philic group are particularly useful in pretreatment formulations in carbon dioxide dry cleaning processes. Without wishing to be bound to any particular theory of the instant invention, it is believed that such surfactants advantageously remain localized in the stained area to which they are applied during the washing cycle and hold water therewith, facilitating cleaning of the stained location. These considerations are separate and distinct from those involved in the selection of a surfactant that does not contain a CO_2-philic group in the cleaning formulation, as noted above.

Additional ingredients can be included depending upon the specific stain that is being treated, in accordance with known formulations.

The pretreatment formulation currently preferred for miscellaneous food and protein stains is a mixture consisting of (%w/w) 74.8% water, 18.5% ISOPAR M™ organic solvent, 1.9% TERGITOL™ 15-S-3 Surfactant; 0.9% TERGITOL™ 15-S-7 surfactant; 0.9% TERGITOL™ 15-S-9 Surfactant, 1% Lipolase, 1% Alcolase, and 1% Temamyl.

The currently preferred tannin specific pretreatment (%w/w) is a mixture consisting of 73.3% water, 18% ISOPAR M™ organic solvent, 1.9% 15-S-3, 0.(% 15-S-7, 0.9% 15-S-9, and 5% glycolic acid.

In another embodiment, a liquid pre-treatment composition useful for carrying out the present invention typically comprises:

(a) water (to balance);

(a) from 30 or 40 percent to 80 percent by volume of an organic co-solvent (preferably a C12-C15 alkane cosolvent);

(b) from 5 or 10 to 40 or 50 percent by volume of d-limonene;

(c) optionally, but preferably, a surfactant as described above (preferably from 0.1 0.5, 1, 2 or 3 percent to 5 or 10 percent total by weight, which may be comprised of one or more different surfactants); and

(d) optionally, water (to balance, typically 0 or 1 to 10, 20 or 40 percent by volume).

Again, the surfactant and organic co-solvent may any of those described above in connection with the cleaning formulations or the surfactant may be a poly(ether-carbonate) copolymer as described below.

The pretreatment formulations can be conveniently provided in a squeeze bottle or spray container for use by dry cleaning personnel and application to garments prior to their being deposited in the dry cleaning apparatus. The pretreatment composition can simply be applied to a stained region of an article to be cleaned, with or without scrubbing or brushing, and the article deposited in the dry cleaning apparatus for subsequent cleaning.

The formulations noted above are useful in aiding the removal of a variety of stains, including spaghetti sauce, some types of pen ink, some types of make-up, coffee, miscellaneous food drippings and miscellaneous bodily fluids. They leave little or no residue on garments relative to commercially available pretreatments, and do not result in undue damage to garments.

The formulations and methods described herein are particularly useful for treating garments, fabrics and the like that have previously been provided with a water or stain-resistant coating, such as described in U.S. Patent No. 6,030,663 to McClain.

<u>3. Poly(ether-carbonate) Copolymers as Pretreatment and Cleaning Surfactants.</u>

A non-fluorine, non-siloxane class of surfactants for CO_2 that show amphiphilic character in CO_2 are poly(ether-carbonate) copolymers. These materials can be derived from the catalytic polymerization of alkylene oxides with CO_2, and are known in the art. *See, e.g.*, T. Sarbu, *Nature* **405**, 165-168 (2000). With catalyst controls amphiphilic poly (ether-carbonate) copolymers with hydrophilic character can be generated as represented by the formula:

$$(-R^1\text{-}O\text{-})x\text{-}(R^2\text{-}O\text{-}CO_2)y$$

Where R^1 and R^2 are each independently alkylene oxide (preferably propylene oxide, ethylene oxide, or hexylene oxide (the R groups can comprise a mixture of the three), and x and y are selected to provide the desired molecular weight as noted below. Such materials may be used as both pretreatment surfactants in the pretreatment formulation disclosed herein or as cleaning surfactants in the carbon dioxide cleaning formulations disclosed herein. Preferred copolymers for use in the present invention have a molecular weight of 200 or 500 to 2,000 or 10,000.

The present invention is explained in greater detail in the following non-limiting examples.

EXAMPLE 1

Carbon Dioxide Dry-Cleaning Composition

An example of a liquid carbon dioxide dry cleaning system that can be used to carry out the present invention is a mixture that contains:

4.2% ISOPAR M™ organic solvent;

0.24% water;

0.196% TRITON™ RW-20 (commercial detergent available from Union Carbide; a secondary amine ethoxylate);

0.048% TRITON™ GR-7M detergent (a commercial detergent of Union Carbide; sodium dioctyl sulfosuccinate in aromatic and aliphatic hydrocarbons)

0.48% TERGITOL™ 15-S-3 detergent (a commercial detergent of Union Carbide; a secondary alcohol ethoxylate); and

liquid carbon dioxide to balance.

EXAMPLE 2

Carbon Dioxide Dry-Cleaning Composition

An additional example of a liquid carbon dioxide dry cleaning system that can be used to carry out the present invention is a mixture that contains:

3.07% ISOPAR M™ organic solvent;

1.32% DPMA (dipropylene glycol monomethyl ether acetate);

0.087% water;

0.023% TRITON™ GR-7M detergent (a commercial detergent of Union Carbide; sodium dioctyl sulfosuccinate in aromatic and aliphatic hydrocarbons)

0.5% TERGITOL™ 15-S-3 detergent (a commercial detergent of Union Carbide; a secondary alcohol ethoxylate); and

liquid carbon dioxide to balance.

EXAMPLE 3

Carbon Dioxide Dry-Cleaning Composition

An additional example of a liquid carbon dioxide dry cleaning system that can be used to carry out the present invention, particularly useful for the cleaning of particulate soil, is a mixture that contains:

4.2% ISOPAR M™ organic solvent;

0.196% TRITON™ RW-20 (commercial detergent available from Union Carbide; a secondary amine ethoxylate);

0.048% TRITON™ GR-7M detergent (a commercial detergent of Union Carbide; sodium dioctyl sulfosuccinate in aromatic and aliphatic hydrocarbons)

0.48% TERGITOL™ 15-S-3 detergent (a commercial detergent of Union Carbide; a secondary alcohol ethoxylate); and

liquid carbon dioxide to balance.

EXAMPLE 4

Carbon Dioxide Dry-Cleaning Composition

An additional example of a liquid carbon dioxide dry cleaning system that can be used to carry out the present invention, also particularly useful for cleaning particulate soil, is a mixture that contains:

3.07% ISOPAR M™ organic solvent;

1.32% DPMA (diopropylene glycol monomethyl ether acetate);

0.023% TRITON™ GR-7M detergent (a commercial detergent of Union Carbide; sodium dioctyl sulfosuccinate in aromatic and aliphatic hydrocarbons)

0.5% TERGITOL™ 15-S-3 detergent (a commercial detergent of Union Carbide; a secondary alcohol ethoxylate); and

liquid carbon dioxide to balance.

EXAMPLE 5

Food and Protein Stain Pretreatment Liquid

The pretreatment formulation currently used for miscellaneous food and protein stains is a mixture consisting of (%w/w) 74.8% water, 18.5% ISOPAR M™ organic solvent, 1.9% TERGITOL™ 15-S-3 Surfactant; 0.9% TERGITOL™ 15-S-7 surfactant; 0.9% TERGITOL™ 15-S-9 Surfactant, 1% Lipolase, 1% Alcolase, and 1% Temamyl. Articles stained with food or protein stains are pretreated with such a composition by squirting or spraying the pretreatment liquid on the stained region, brushing if desired, and depositing the article in a cleaning apparatus for subsequent cleaning with a composition as described in Examples 1-4 above.

EXAMPLE 6

Food and Protein Stain Pretreatment Liquid

The current tannin specific pretreatment (%w/w) is a mixture consisting of 73.3% water, 18% ISOPAR M™ organic solvent, 1.9% 15-S-3, 0.(% 15-S-7, 0.9% 15-S-9, and 5% glycolic acid. Articles stained with food or protein stains are pretreated with such a composition by squirting or spraying the pretreatment liquid on the stained region, brushing if desired, and depositing the article in a cleaning apparatus for subsequent cleaning with a composition as described in Examples 1-4 above.

EXAMPLES 7-13

Pretreatments with Poly(ether-carbonate)

Copolymers and D-limonene

EXAMPLE 7

A pretreatment formulation consisting of 10% of a triblock copolymer as represented above, 3% Tergitol 15-S-3 and 87% water is delivered to a swatch stained with grape juice. The swatch is then cleaned in a liquid CO_2 dry cleaning process such as the MICARE® cleaning process (available from Micell, Inc., 7516 Precision

Drive, Raleigh, North Carolina USA 27613). Once retrieved, the soil is determined to be about 95% removed (by weight) compared to about 25% for a similar soil swatch cleaned but not pretreated.

EXAMPLE 8

A pretreatment formulation consisting of 10% of a polymer derived from the catalytically controlled polymerization of propylene oxide and CO_2, 25% of d-limonene, and 65% of a C12 to C15 aliphatic hydrocarbon is sprayed onto a swatch that is soiled with a heavy industrial grease with dark particulate. The swatch is then cleaned in the MICARE® cleaning process and once removed the soil is determined to be about 98% removed. This compares to 60% removal on a swatch cleaned but not pretreated.

EXAMPLE 9

A pretreatment formulation consisting of 60% aliphatic hydrocarbon composed of C12 to C15 materials, 35% d-limonene, and 5% Tergitol 15-s-3 is applied liberally to a grease stain on a textile. The textile is then cleaned using the MICARE® process. After completion of the process, the soil is substantially completely removed.

EXAMPLE 10

A pretreatment formulation comprises a mixture as follows:

75% Water;

19% ISOPAR M® aliphatic hydrocarbon cosolvent (C12-C15);

2% DPMA (dipropylene glycol methyl ether acetate)

2% Tergitol 15-S-3

2% of a copolymer generated from the radical copolymerization of a 1,1,2,2,-tetrahydroperfluoroalkyl acrylate, Polyethylene glycol methacrylate, butyl acrylate, and steryl acrylate in a molar ratio of (0.5, 0.3, 1, 1)

The formulation is applied to a combination of protein and tannin based soils that were pre-applied to several fabrics. The fabrics were then cleaned in the MICARE® cleaning system and the stains were evaluated versus similar stains cleaned but not pretreated with the formulation. The non-pretreated stains were

determined to be about 10 to 50% removed after the cleaning process. The pretreated stains were about 40 to 100% removed after the cleaning process.

EXAMPLE 11

A pretreatment formulation comprises a mixture as follows:

75% Water;

19% C12-C15 Aliphatic hydrocarbon cosolvent;

2% Ether or ester capped alkylene oxide cosolvent (DPM-dipropylene glycol monomethyl ether, DPMA- dipropylene glycol methyl ether acetate);

2% Alkyl/alkylene oxide block A/B non-ioinc surfactant (15-s-3, 15-s-5, 15-s-7, Neodol, etc.); and

2% of a copolymer generated by the radical copolymerization of a 1,1,2,2,-tetrahydroperfluoroalkyl acrylate, a lipophilic comonomer, and a hydrophilic comonmer.

EXAMPLE 12

A pretreatment formulation comprises a mixture as follows:

75% Water;

21% Isopar M hydrocarbon cosolvent;

2% Tergitol 15-S-3 surfactant; and

2% PDMS-PEG (MW = 600g/mol) Polydimethyl Siloxane-Polyethylene glycol block copolymer.

The formulation is applied to a combination of protein and tannin based soils that were pre-applied to several fabrics. The fabrics were then cleaned in the MICARE® dry cleaning system (available from Micell Technologies Inc., 7516 Precision Drive, Raleigh, NC27613) and the stains were evaluated versus similar stains cleaned but not pretreated with the formulation. The non-pretreated stains were determined to be 10 to 50% removed after the cleaning process. The pretreated stains were 60to 100% removed after the cleaning process.

EXAMPLE 13

A pretreatment formulation comprises a mixture as follows:

75% water

21% Aliphatic hydrocarbon (C12-C15)

2% Alkyl/alkylene oxide block A/B non-ioinc surfactant (15-s-3, 15-s-5, 15-s-7, Neodol, etc.)

2% PDMS-Polyalkylene oxide copolymer (polyalkyl= ethylene, propylene)

EXAMPLES 14-15

Detergent formulation for CO2 dry cleaning

EXAMPLE 14

A poly (ether-carbonate) copolymer as described above is added to a liquid CO_2 dry cleaning apparatus at a concentration of 1.0% along with water at 0.40% and CO_2 at 98.6%. A swatch containing a water soluble food dye is added to a rotating cleaning drum along with other fabric pieces. The liquid mixture is then circulated through the cleaning drum and additional water is added to the circulating fluid to bring the water concentration up to 0.80%. After a period of 10 minutes with adequate circulation and agitation, the liquid is drained and the swatch is removed. Essentially one hundred percent of the food dye was removed from the fabric.

EXAMPLE 15

A poly(ether-carbonate) copolymer as described above is added to a liquid CO_2 dry cleaning apparatus at a concentration of 1.0% along with water at 0.40%, an aliphatic hydrocarbon cosolvent at 2%, and CO_2 at 96.6%. A swatch containing a water soluble food dye is added to a rotating cleaning drum along with other fabric pieces. The liquid mixture is then circulated through the cleaning drum and additional water is added to the circulating fluid to bring the water concentration up to 0.80%. After a period of 10 minutes with adequate circulation and agitation, the liquid is drained and the swatch is removed. Essentially one –hundred percent of the food dye was removed from the fabric.

The foregoing is illustrative of the present invention, and is not to be construed as limiting thereof. The invention is defined by the following claims, with equivalents of the claims to be included therein.

That which is claimed is:

1. A method for dry-cleaning garments or fabrics in carbon dioxide, said garment or fabric including a stained portion, said method comprising:

pretreating said stained portion with a liquid pretreatment composition, said composition containing a pretreatment surfactant, wherein said pretreatment surfactant does not contain a CO_2-philic group;

contacting said article with a liquid dry cleaning composition for a time sufficient to clean the article, said liquid dry-cleaning composition comprising a mixture of carbon dioxide and a cleaning surfactant; and then

separating the article from the liquid dry cleaning composition.

2. A method according to claim 1, wherein said pretreatment composition is an aqueous composition.

3. A method according to claim 1, wherein said pretreatment composition is a homogeneous composition.

4. A method according to claim 1, wherein said pretreatment composition is a heterogeneous composition.

5. A method according to claim 1, wherein said liquid dry cleaning composition is at a temperature of 0° C to 30° C.

6. A method according to claim 1, said pretreatment composition further comprising an organic co-solvent.

7. A method according to claim 1, said pretreatment composition further comprising a C12-C15 alkane cosolvent.

8. A method according to claim 1, wherein said contacting step is carried out by jet agitation.

9. A method for dry-cleaning garments or fabrics in carbon dioxide, said garment or fabric including a stained portion, said method comprising:

(a) pretreating said stained portion with a liquid pretreatment composition, said composition containing a pretreatment surfactant, wherein said pretreatment surfactant does not contain a CO_2-philic group;

(b) combining a garment or fabric article to be cleaned and a liquid dry cleaning composition in a closed drum so that said closed drum contains both a liquid phase and a vapor phase, said liquid dry cleaning composition comprising a mixture of liquid carbon dioxide and a cleaning surfactant;

(c) agitating said article in said drum so that said article contacts both said liquid dry cleaning composition and said vapor phase for a time sufficient to clean said article; and then

(d) removing the cleaned article from said drum.

10. A method according to claim 9, wherein said pretreatment composition is an aqueous composition.

11. A method according to claim 9, wherein said pretreatment composition is a homogeneous composition.

12. method according to claim 9, wherein said pretreatment composition is a heterogeneous composition.

13. A method according to claim 9, wherein said drum is a horizontal rotating drum, and said agitating step is carried out by rotating said drum.

14. A method according to claim 9, wherein said drum is a vertical drum having an agitator positioned therein, and said agitating step is carried out by moving said agitator.

15. A method according to claim 9, wherein said pretreatment composition further comprises an organic cosolvent.

16. A method according to claim 9, wherein said pretreatment composition further comprises a C12-C15 alkane cosolvent.

17. A method for dry-cleaning garments or fabrics in carbon dioxide, said garment or fabric including a stained portion, said method comprising:

pretreating said stained portion with a liquid pretreatment composition, wherein said composition comprises 5 to 75% by volume d-limonene;

contacting said article with a liquid dry cleaning composition for a time sufficient to clean the article, said liquid dry-cleaning composition comprising a mixture of carbon dioxide and a cleaning surfactant; and then

separating the article from the liquid dry cleaning composition.

18. A method according to claim 17, wherein said pretreatment composition is an aqueous composition.

19. A method according to claim 17, wherein said pretreatment composition is a homogeneous composition.

20. A method according to claim 17, wherein said pretreatment composition is a heterogeneous composition.

21. A method according to claim 17, said pretreatment composition further comprising an organic co-solvent.

22. A method according to claim 17, said pretreatment composition further comprising a C12-C15 alkane co-solvent; wherein

said limonine is included in an amount of from 5 to 40 percent by volume; and

said alkane co-solvent is included in an amount of 30 to 80 percent by volume.

23. A method according to claim 22, said pretreatment composition further comprising 1 to 10 percent by weight of surfacatant.

24. A method for dry-cleaning garments or fabrics in carbon dioxide, said garment or fabric including a stained portion, said method comprising:

(a) pretreating said stained portion with a liquid pretreatment composition, said composition containing a pretreatment surfactant, wherein said composition comprises 5 to 75 percent by volume of d-limonene;

(b) combining a garment or fabric article to be cleaned and a liquid dry cleaning composition in a closed drum so that said closed drum contains both a liquid phase and a vapor phase, said liquid dry cleaning composition comprising a mixture of liquid carbon dioxide and a cleaning surfactant;

(c) agitating said article in said drum so that said article contacts both said liquid dry cleaning composition and said vapor phase for a time sufficient to clean said article; and then

(d) removing the cleaned article from said drum.

25. A method according to claim 24, wherein said pretreatment composition is an aqueous composition.

26. A method according to claim 24, wherein said pretreatment composition is a homogeneous composition.

27. A method according to claim 24, wherein said pretreatment composition is a heterogeneous composition.

28. A method according to claim 24, wherein said drum is a horizontal rotating drum, and said agitating step is carried out by rotating said drum.

29. A method according to claim 24, wherein said drum is a vertical drum having an agitator positioned therein, and said agitating step is carried out by moving said agitator.

30. A method according to claim 24, wherein said liquid dry cleaning composition is a room-temperature composition and said agitating step is carried out at a temperature of 0° C to 30° C.

31. A method according to claim 24, wherein said pretreatment composition further comprises an organic co-solvent.

32. A method according to claim 24, said pretreatment composition further comprising a C12-C15 alkane co-solvent; wherein

said limonine is included in an amount of from 5 to 40 percent by volume; and

said alkane co-solvent is included in an amount of 30 to 80 percent by volume.

33. A method according to claim 32, said pretreatment composition further comprising 1 to 10 percent by weight of surfactant.

34. A method for dry-cleaning garments or fabrics in carbon dioxide, said garment or fabric including a stained portion, said method comprising:

pretreating said stained portion with a liquid pretreatment composition, said composition containing a pretreatment surfactant, wherein said pretreatment surfactant comprises a poly(ether-carbonate) copolymer;

contacting said article with a liquid dry cleaning composition for a time sufficient to clean the article, said liquid dry-cleaning composition comprising a mixture of carbon dioxide and a cleaning surfactant; and then

separating the article from the liquid dry cleaning composition.

35. A method according to claim 34, wherein said pretreatment composition is an aqueous composition.

36. A method according to claim 34, wherein said pretreatment composition is a homogeneous composition.

37. A method according to claim 34, wherein said pretreatment composition is a heterogeneous composition.

38. A method according to claim 34, wherein said liquid dry cleaning composition is at a temperature of 0° C to 30° C.

39. A method according to claim 34, said pretreatment composition further comprising an organic co-solvent.

40. A method according to claim 34, said pretreatment composition further comprising a C12-C15 alkane cosolvent. .

41. A method according to claim 1, wherein said contacting step is carried out by jet agitation.

42. A method for dry-cleaning garments or fabrics in carbon dioxide, said garment or fabric including a stained portion, said method comprising:

(a) pretreating said stained portion with a liquid pretreatment composition, said composition containing a pretreatment surfactant, wherein said pretreatment surfactant comprises a poly (ether-carbonate copolymer);

(b) combining a garment or fabric article to be cleaned and a liquid dry cleaning composition in a closed drum so that said closed drum contains both a liquid phase and a vapor phase, said liquid dry cleaning composition comprising a mixture of liquid carbon dioxide and a cleaning surfactant;

(c) agitating said article in said drum so that said article contacts both said liquid dry cleaning composition and said vapor phase for a time sufficient to clean said article; and then

(d) removing the cleaned article from said drum.

43. A method according to claim 42, wherein said pretreatment composition is an aqueous composition.

44. A method according to claim 42, wherein said pretreatment composition is a homogeneous composition.

45. A. method according to claim 42, wherein said pretreatment composition is a heterogeneous composition.

46. A method according to claim 42, wherein said drum is a horizontal rotating drum, and said agitating step is carried out by rotating said drum.

47. A method according to claim 42, wherein said drum is a vertical drum having an agitator positioned therein, and said agitating step is carried out by moving said agitator.

48. A method according to claim 42, wherein said liquid dry cleaning composition is a room-temperature composition and said agitating step is carried out at a temperature of 0° C to 30° C.

49. A method according to claim 42, wherein said pretreatment composition further comprises an organic cosolvent.

50. A method according to claim 42, wherein said pretreatment composition further comprises a C12-C15 alkane cosolvent.

51. A method for dry-cleaning garments or fabrics in carbon dioxide, said garment or fabric including a stained portion, said method comprising:

pretreating said stained portion with a liquid pretreatment composition, said composition containing a pretreatment surfactant, wherein said pretreatment surfactant contains a CO_2-philic group, said CO_2-philic group selected from the group consisting of fluorine-containing segments and siloxane containing segments;

contacting said article with a liquid dry cleaning composition for a time sufficient to clean the article, said liquid dry-cleaning composition comprising a mixture of carbon dioxide and a cleaning surfactant; and then

separating the article from the liquid dry cleaning composition.

52. A method according to claim 51, wherein said pretreatment composition is an aqueous composition.

53. A method according to claim 51, wherein said pretreatment composition is a homogeneous composition.

54. A method according to claim 51, wherein said pretreatment composition is a heterogeneous composition.

55. A method according to claim 51, said pretreatment composition further comprising an organic co-solvent.

56. A method according to claim 51, said pretreatment composition further comprising a C12-C15 alkane cosolvent.

57. A method according to claim 51, wherein said contacting step is carried out by jet agitation.

58. A method for dry-cleaning garments or fabrics in carbon dioxide, said garment or fabric including a stained portion, said method comprising:

(a) pretreating said stained portion with a liquid pretreatment composition, said composition containing a pretreatment surfactant, wherein said pretreatment surfactant contains a CO_2-philic group, said CO_2-philic group selected from the group consisting of fluorine-containing segments and siloxane containing segments;

(b) combining a garment or fabric article to be cleaned and a liquid dry cleaning composition in a closed drum so that said closed drum contains both a liquid phase and a vapor phase, said liquid dry cleaning composition comprising a mixture of liquid carbon dioxide and a cleaning surfactant;

(c) agitating said article in said drum so that said article contacts both said liquid dry cleaning composition and said vapor phase for a time sufficient to clean said article; and then

(d) removing the cleaned article from said drum.

59. A method according to claim 58, wherein said pretreatment composition is an aqueous composition.

60. A method according to claim 58, wherein said pretreatment composition is a homogeneous composition.

61. method according to claim 58, wherein said pretreatment composition is a heterogeneous composition.

62. A method according to claim 58, wherein said drum is a horizontal rotating drum, and said agitating step is carried out by rotating said drum.

63. A method according to claim 58, wherein said drum is a vertical drum having an agitator positioned therein, and said agitating step is carried out by moving said agitator.

64. A method according to claim 58, wherein said liquid dry cleaning composition is a room-temperature composition and said agitating step is carried out at a temperature of 0° C to 30° C.

65. A method according to claim 58, wherein said pretreatment composition further comprises an organic cosolvent.

66. A method according to claim 48, wherein said pretreatment composition further comprises a C12-C15 alkane cosolvent.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/19790

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :D06L 01/00, 01/02; B05D 01/00; C11D 1/82, 3/39, 3/43;
US CL :Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 8/142, 137, 158; 510/285, 286, 289, 291, 291, 405; 134/10, 21, 30; 427/389.9;

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST PATENT SEARCH DATABASE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,858,022 A (ROMACK et al) 12 January 1999, see abstract.	1-66
A	US 5,370,742 A (MITCHELL et al) 06 December 1994, see abstract.	1-66
A,P	US 6,030,663 A (MCCLAIN et al) 29 February 2000, see abstract.	1-66
A	US 5,683,977 A (JURELLER et al) 04 November 1997, see abstract.	1-66

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/19790

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

8/142, 137, 158; 510/285, 286, 289, 291, 291, 405; 134/10, 21, 30; 427/389.9:

Dry cleaning methods and compositions

Publication number: JP2001514337T

Publication date: 2001-09-11

Inventor:

Applicant:

Classification:

- international: ***C11D3/04; D06L1/00; D06L1/02; D06L1/04; D06L1/12;*** **C11D3/04; D06L1/00;** (IPC1-7): C11D3/04; D06L1/00; D06L1/02; D06L1/04; D06L1/12

- European: D06L1/00; D06L1/04

Application number: JP20000507884T 19980827

Priority number(s): US19970921620 19970827; WO1998US17730 19980827

Also published as:

WO9910585 (A1)
EP1007779 (A1)
US5858022 (A1)
EP1007779 (A0)
CA2301636 (A1)

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Abstract not available for JP2001514337T
Abstract of corresponding document: **US5858022**

A method for dry-cleaning articles such as fabrics and clothing in carbon dioxide comprises contacting an article to be cleaned with a liquid dry cleaning composition for a time sufficient to clean the fabric. The liquid dry-cleaning composition comprises a mixture of carbon dioxide, water, a surfactant, and an organic co-solvent. After the contacting step, the article is separated from the liquid dry cleaning composition. The method is preferably carried out at ambient temperature. The surfactant may be either one that contains a CO2-philic group or one that does not contain a CO2-philic group. The organic co-solvent is preferably an alkane that has a flash point above 140 DEG F.

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
D06L 1/00, C11D 1/00, D06L 1/02, 1/04, 1/12

A1

(11) International Publication Number: **WO 99/10585**

(43) International Publication Date: 4 March 1999 (04.03.99)

(21) International Application Number: PCT/US98/17730

(22) International Filing Date: 27 August 1998 (27.08.98)

(30) Priority Data:
08/921,620 27 August 1997 (27.08.97) US

(63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application
US Not furnished (CON)
Filed on Not furnished

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(81) Designated States: AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: DRY CLEANING METHODS AND COMPOSITIONS

(57) Abstract

A method for dry–cleaning articles such as fabrics and clothing in carbon dioxide comprises contacting an article to be cleaned with a liquid dry cleaning composition for a time sufficient to clean the fabric. The liquid dry–cleaning composition comprises a mixture of carbon dioxide, water, a surfactant, and an organic co–solvent. After the contacting step, the article is separated from the liquid dry cleaning composition. The method is preferably carried out at ambient temperature. The surfactant is preferably one that does not contain a CO_2–philic group. The organic co–solvent is preferably an alkane and has a flash point above 140 °F.

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DRY CLEANING METHODS AND COMPOSITIONS

This application is a continuation-in-part of commonly owned, copending patent application Serial No. 08/921,620, filed August 27, 1997, the disclosure of which is incorporated by reference herein in its entirety.

Field of the Invention

The present invention relates to methods and compositions for carrying out the dry-cleaning of fabrics (*e.g.*, garments) in liquid carbon dioxide.

Background of the Invention

Commercial dry cleaning systems currently employ potentially toxic and environmentally harmful halocarbon solvents, such as perchloroethylene. Carbon dioxide has been proposed as an alternative to such systems in U.S. Patent No. 4,012,194 to Maffei. A problem with carbon dioxide is, however, its lower solvent power relative to ordinary solvents.

German Patent Application DE3904514 A1, published August 23, 1990, describes a cleaning system combining various conventional anionic or nonionic surface active agents with supercritical CO_2. The system described therein appears to combine the detergency mechanism of conventional surface active agents with the solvent power of supercritical fluid carbon dioxide. A carbon dioxide dry cleaning system effective for liquid carbon dioxide is not provided.

U.S. Patent No. 5,683,473 to Jureller et al. (see also 5,683,977 to Jureller et al.) describes a dry cleaning system utilizing carbon dioxide in liquid form in combination with surfactants that contain a functional moiety that is CO_2-philic,

which surfactants are not conventionally used for detergent cleaning. Since there are numerous advantages to employing conventional surfactants (*e.g.*, cost, ready availability, established regulatory approval, established toxicology, etc), it would be extremely desireable to have a dry cleaning system for liquid carbon dioxide that employs conventional surfactants that do not contain a CO_2-philic group.

U.S. Patent No. 5,377,705 to Smith et al. describes a precision cleaning system in which a work piece is cleaned with a mixture of CO_2 and a co-solvent. Smith provides an entirely non-aqueous system, stating: "The system is also designed to replace aqueous or semi-aqueous based cleaning processes to eliminate the problems of moisture damage to parts and water disposal" (col. 4 line 68 to col. 5 line 3). Co-solvents that are listed include acetone and ISOPAR™ M (col. 8, lines 19-24). Use in dry cleaning is neither suggested nor disclosed. Indeed, since some water must be present in dry-cleaning, such use is contrary to this system.

In view of the foregoing, there is a continuing need for effective carbon dioxide-based dry cleaning systems.

Summary of the Invention

A method for dry-cleaning articles such as fabrics and clothing in carbon dioxide comprises contacting an article to be cleaned with a liquid dry cleaning composition for a time sufficient to clean the fabric. The liquid dry-cleaning composition comprises a mixture of carbon dioxide, water, a surfactant, and an organic co-solvent. After the contacting step, the article is separated from the liquid dry cleaning composition.

Preferably, the liquid dry cleaning composition is at ambient temperature, of about 0° C to 30° C. The surfactant is soluble in the co-solvent. The surfactant may or may not be soluble in the CO_2. Hence, in one embodiment; the surfactant may contain a CO_2-philic group. However, in the preferred embodiment, the surfactant does not contain a CO_2-philic group. Hence, an advantage of the present invention is that, by proper use of the co-solvent, conventional surfactants may be employed in a liquid carbon dioxide dry cleaning system.

Detailed Description of the Invention

The term "clean" as used herein refers to any removal of soil, dirt, grime, or other unwanted material, whether partial or complete. The invention may be used to clean nonpolar stains (*i.e.*, those which are at least partially made by nonpolar organic compounds such as oily soils, sebum and the like), polar stains (*i.e.*, hydrophilic stains such as grape juice, coffee and tea stains), compound hydrophobic stains (*i.e.*, stains from materials such as lipstick and candle wax), and particulare soils (*i.e.*, soils containing insoluble solid components such as silicates, carbon black, etc.).

Articles that can be cleaned by the method of the present invention are, in general, garments and fabrics (including woven and non-woven) formed from materials such as cotton, wool, silk, leather, rayon, polyester, acetate, fiberglass, furs, etc., formed into items such as clothing, work gloves, rags, leather goods (*e.g.*, handbags and brief cases), etc.

Liquid dry-cleaning compositions useful for carrying out the present invention typically comprise:

(a) from 0.02, 0.05 or 0.1 to 5 or 10 percent (more preferably from .1 to 4 percent) water;

(b) carbon dioxide (to balance; typically at least 30 percent);

(c) surfactant (preferably from 0.1 or .5 percent to 5 or 10 percent total, which may be comprised of one or more different surfactants); and

(d) from 0.1 to 50 percent (more preferably 1, 2 or 4 percent to 30 percent) of an organic co-solvent.

Percentages herein are expressed as percentages by weight unless otherwise indicated.

The composition is provided in liquid form at ambient, or room, temperature, which will generally be between zero and 50° Centigrade. The composition is held at a pressure that maintains it in liquid form within the specified temperature range. The cleaning step is preferably carried out with the composition at ambient temperature.

The organic co-solvent is, in general, a hydrocarbon co-solvent. Typically the co-solvent is an alkane co-solvent, with C_{10} to C_{20} linear, branched, and cyclic alkanes, and mixtures thereof (preferably saturated) currently preferred. The organic co-solvent preferably has a flash point above 140°F, and more preferably has a flash point above 170°F. The organic co-solvent may be a mixture of compounds, such as

mixtures of alkanes as given above, or mixtures of one or more alkanes. Additional compounds such as one or more alcohols (*e.g.*, from 0 or 0.1 to 5% of a C1 to C15 alcohol (including diols, triols, etc.)) different from the organic co-solvent may be included with the organic co-solvent.

Examples of suitable co-solvents include, but are not limited to, aliphatic and aromatic hydrocarbons, and esters and ethers thereof, particularly mono and di-esters and ethers (*e.g.*, EXXON ISOPAR L, ISOPAR M, ISOPAR V, EXXON EXXSOL, EXXON DF 2000, CONDEA VISTA LPA-170N, CONDEA VISTA LPA-210, cyclohexanone, and dimethyl succinate), alkyl and dialkyl carbonates (*e.g.*, dimethyl carbonate, dibutyl carbonate, di-t-butyl dicarbonate, ethylene carbonate, and propylene carbonate), alkylene and polyalkylene glycols, and ethers and esters thereof (*e.g.*, ethylene glycol-n-butyl ether, diethylene glycol-n-butyl ethers, propylene glycol methyl ether, dipropylene glycol methyl ether, tripropylene glycol methyl ether, and dipropylene glycol methyl ether acetate), lactones (*e.g.*, (gamma)butyrolactone, (epsilon)caprolactone, and (delta) dodecanolactone), alcohols and diols (*e.g.*, 2-propanol, 2-methyl-2-propanol, 2-methoxy-2-propanol, 1-octanol, 2-ethyl hexanol, cyclopentanol, 1,3-propanediol, 2,3-butanediol, 2-methyl-2,4-pentanediol) and polydimethylsiloxanes (*e.g.*, decamethyltetrasiloxane, decamethylpentasiloxane, and hexamethyldisloxane), etc.

Any surfactant can be used to carry out the present invention, including both surfactants that contain a CO_2-philic group (such as described in PCT Application WO96/27704) linked to a CO_2-phobic group (*e.g.*, a lipophilic group) and (more preferably) surfactants that do not contain a CO_2-philic group (*i.e.*, surfactants that comprise a hydrophilic group linked to a hydrophobic (typically lipophilic) group). A single surfactant may be used, or a combination of surfactants may be used.

Numerous surfactants are known to those skilled in the art. *See, e.g.*, McCutcheon's Volume 1: Emulsifiers & Detergents (1995 North American Edition) (MC Publishing Co., 175 Rock Road, Glen Rock, NJ 07452). Examples of the major surfactant types that can be used to carry out the present invention include the: alcohols, alkanolamides, alkanolamines, alkylaryl sulfonates, alkylaryl sulfonic acids, alkylbenzenes, amine acetates, amine oxides, amines, sulfonated amines and amides, betaine derivatives, block polymers, carboxylated alcohol or alkylphenol ethoxylates,

carboxylic acids and fatty acids, diphenyl sulfonate derivatives, ethoxylated alcohols, ethoxylated alkylphenols, ethoxylated amines and/or amides, ethoxylated fatty acids, ethoxylated fatty esters and oils, fatty esters, fluorocarbon-based surfactants, glycerol esters, glycol esters, hetocyclic-type products, imidazolines and imidazoline derivatives, isethionates, lanolin-based derivatives, lecithin and lecithin derivatives, lignin and lignin deriviatives, maleic or succinic anhydrides, methyl esters, monoglycerides and derivatives, olefin sulfonates, phosphate esters, phosphorous organic derivatives, polyethylene glycols, polymeric (polysaccharides, acrylic acid, and acrylamide) surfactants, propoxylated and ethoxylated fatty acids alcohols or alkyl phenols, protein-based surfactants, quaternary surfactants, sarcosine derivatives, silicone-based surfactants, soaps, sorbitan derivatives, sucrose and glucose esters and derivatives, sulfates and sulfonates of oils and fatty acids, sulfates and sulfonates, ethoxylated alkylphenols, sulfates of alcohols, sulfates of ethoxylated alcohols, sulfates of fatty esters, sulfonates of benzene, cumene, toluene and xylene, sulfonates of condensed naphthalenes, sulfonates of dodecyl and tridecylbenzenes, sulfonates of naphthalene and alkyl naphthalene, sulfonates of petroleum, sulfosuccinamates, sulfosuccinates and derivatives, taurates, thio and mercapto derivatives, tridecyl and dodecyl benzene sulfonic acids, etc.

Additional examples of surfactants that can be used to carry out the present invention include alcohol and alkylphenol polyalkyl ethers(*e.g.*, TERGITOL 15-S-3™ secondary alcohol ethoxylate, TRITON X-207™ dinonylphenol ethoxylate, NEODOL 91-2.5™ primary alcohol ethoxylate, RHODASURF BC-410™ isotridecyl alcohol ethoxylate, RHODASURF DA-630™ tridecyl alcohol ethoxylate) alkylaryl carbonates, including salts and derivatives thereof (*e.g.*, acetic acid, MARLOWET 4530™ dialkylphenol polyethylene glycol acetic acid, MARLOWET 1072™ alkyl polyethylene glycol ether acetic acid), alkoxylated fatty acids (*e.g.*, NOPALCOL 1-TW™ diethylene glycol monotallowate, TRYDET 2600™ polyoxyethylene (8) monostearate), alkylene oxide block copolymers (*e.g.*, PLURONIC™ and TETRONIC™ products), acetylenic alcohols and diols (*e.g.*, SURFYNOL™ and DYNOL™ products), mono- and di-esters of sulfosuccinic acid (*e.g.*, AEROSOL OT™ sodium dioctyl sulfosuccinate, AEROSOL IB-45™ sodium diisobutyl sulfosuccinate, MACKANATE DC-50™ dimethicone copolyol disodium

sulfosuccinate, SOLE TERGE-8™ oleic acid isopropanolamide monoester of sodium sulfosuccinate), sulfosuccinamic acid and esters thereof (*e.g.* AEROSOL 18™ disodium-N-octadecyl sulfosucciniamate, AEROSOL 22™ tetrasodium N-(1,2-dicarboxyethyl)-N octadecyl sulfosuccinamate) sorbitan esters including derivatives thereof (*e.g.*, SPAN 80™ sorbitan monoleate, ALKAMULS 400-DO™ sorbitan dioleate, ALKAMULS STO™ sorbitan trioleate, TWEEN 81™ polyoxyethylene (5) sorbitan monoleate, TWEEN 21™ polyoxyethylene (4) sorbitan monolaurate), isothionates including derivatives thereof (*e.g.*, GEROPON AC-270™ sodium cocoyl isothionate), polymeric alkylaryl compounds and lignins, including derivatives thereof (*e.g.*, LIGNOSITE 50™ calcium lignosulfonate), alkylaryl sulfonic acids and salts thereof (*e.g.*, CALIMULSE EM-99™ branched dodecylbenzene sulfonic acid, WITCONATE C-50H™ sodium dodecylbenzene sulfonate, WITCONATE P10-59™ amine salt of dodecylbenzene sulfonate), sulfonated amines and amides (*e.g.*, CALIMULSE PRS™ isopropylamine sulfonate), Betaine and sultaine derivatives, and salts thereof (*e.g.*, lauryl sulfobetaine, dodecyldimethyl(3-sulfopropyl)ammonium hydroxide, FOAMTAIN CAB-A™ cocamidopropyl betaine ammonium salt, FOAMTAINE SCAB™ cocamidopropyl hydroxy sultaine), *e.g.*, imidazolines including derivatives thereof (*e.g.*, MONOAZOLINE O™ substituted imidazoline of oleic acid, MONOAZOLINE T™ substituted imidazoline of Tall Oil), oxazolines including derivatives thereof (*e.g.*, ALKATERGE E™ oxazoline derivative, ALKATERGE T-IV™ ethoxylated oxazoline derivative), carboxylated alcohol or alkylphenol ethoxylates including derivatives thereof (*e.g.*, MARLOSOL OL7™ oleic acid polyglycol ester), diphenyl sulfonates including derivatives thereof (*e.g.*, DOWFAX™ detergent diphenyl oxide disulfonate, DOWFAX™ dry detergent: sodium n-hexadecyl diphenyl oxide disulfonate, DOWFAX™ Dry hydrotrope: sodium hexyl diphenyloxide disulfonate) fluorinated surfactants (*e.g.*, FLUORAD FC-120™ ammonium perfluoroalkyl sulfonate, FLUORAD FC-135™ fluoroalkyl quaternary ammonium iodides, FLUORAD FC-143™ ammonium perfluoroalkyl carboxylates), lecithins including lecithin derivatives (*e.g.*, ALCOLEC BS™ soy phosphatides), phosphate esters (*e.g.*, ACTRAFOS SA-216™ aliphatic phosphate ester, ACTRAFOS 110™ phosphate ester of complex aliphatic hydroxyl compound, CHEMPHOS TC-310™ aromatic phosphate ester, CALGENE PE-112N™

phosphated mono- and diglycerides), sulfates and sulfonates of fatty acids (*e.g.*, ACTRASOL PSR™ sulfated castor oil, ACTRASOL SR75™ sulfated oleic acid), sulfates of alcohols (*e.g.*, DUPONOL C™ sodium lauryl sulfate, CARSONOL SHS™ sodium 2-ethyl-1-hexyl sulfate, CALFOAM TLS-40™ triethanolamine lauryl sulfate), sulfates of ethoxylated alcohols (*e.g.*, CALFOAM ES-301™ sodium lauryl ether sulfate), amines, including salts and derivatives thereof (*e.g.*, Tris(hydroxymethyl)aminomethane, ARMEEN™ primary alkylamines, ARMAC HT™ acetic acid salt of N-alkyl amines) amide sulfonates (*e.g.*, GEROPON TC-42™ sodium N-coconut acid-N-methyl taurate, GEROPON TC 270™ sodium cocomethyl tauride), quaternary amines, including salts and derivatives thereof (*e.g.*, ACCOSOFT 750™ methyl bis (soya amidoethyl)-N-polyethoxyethanol quaternary ammonium methyl sulfate, ARQUAD™ N-alkyl trimethyl ammonium chloride, ABIL QUAT 3272™ diquaternary polydimethylsiloxane), amine oxides (*e.g.*, AMMONYX CO™ cetyl dimethylamine oxide, AMMONYX SO™ stearamine oxide), esters of glycerol, sucrose, glucose, sarcosine and related sugars and hydrocarbons including their derivatives (*e.g.*, GLUCATE DO™ methyl glucoside dioleate, GLICEPOL 180™ glycerol oleate, HAMPOSYL AL-30™ ammonium lauroyl sarcosinate, HAMPOSYL M™ N-myristoyl sarcosine, CALGENE CC™ propylene glycol dicaprylate/dicaprate), polysaccharides including derivatives thereof (*e.g.*, GLUCOPON 225 DK™ alkyl polysaccharide ether), protein surfactants (*e.g.*, AMITER LGS-2™ dioxyethylene stearyl ether diester of N-lauroyl-L-glutamic acid, AMISOFT CA™ cocoyl glutamic acid, AMISOFT CS 11™ sodium cocoyl glutamate, MAYTEIN KTS™ sodium/TEA lauryl hydrolyzed keratin, MAYPON 4C™ potassium cocoyl hydrolyzed collagen), and including thio and mercapto derivatives of the foregoing (*e.g.*, ALCODET™ polyoxyethylene thioether, BURCO TME™ ethoxylated dodecyl mercaptan), etc.

Thus the present invention may be carried out using conventional surfactants, including but not limited to the anionic or nonionic alkylbenzene sulfonates, ethoxylated alkylphenols and ethoxylated fatty alcohols described in Schollmeyer German Patent Application DE 39 04514 A1, that are not soluble in liquid carbon dioxide and which could not be utilized in the invention described in U.S. Patent No. 5,683,473 to Jureller et al. or U.S. Patent No. 5,683,977 to Jureller et al.

As will be apparent to those skilled in the art, numerous additional ingredients can be included in the dry-cleaning composition, including detergents, bleaches, whiteners, softeners, sizing, starches, enzymes, hydrogen peroxide or a source of hydrogen peroxide, fragrances, etc.

In practice, in a preferred embodiment of the invention, an article to be cleaned and a liquid dry cleaning composition as given above are combined in a closed drum. The liquid dry cleaning composition is preferably provided in an amount so that the closed drum contains both a liquid phase and a vapor phase (that is, so that the drum is not completely filled with the article and the liquid composition). The article is then agitated in the drum, preferably so that the article contacts both the liquid dry cleaning composition and the vapor phase, with the agitation carried out for a time sufficient to clean the fabric. The cleaned article is then removed from the drum. The article may optionally be rinsed (for example, by removing the composition from the drum, adding a rinse solution such as liquid CO_2 (with or without additional ingredients such as water, co-solvent, etc.) to the drum, agitating the article in the rinse solution, removing the rinse solution, and repeating as desired), after the agitating step and before it is removed from the drum. The dry cleaning compositions and the rinse solutions may be removed by any suitable means, including both draining and venting.

Any suitable cleaning apparatus may be employed, including both horizontal drum and vertical drum apparatus. When the drum is a horizontal drum, the agitating step is carried out by simply rotating the drum. When the drum is a vertical drum it typically has an agitator positioned therein, and the agitating step is carried out by moving (*e.g.*, rotating or oscillating) the agitator within the drum. A vapor phase may be provided by imparting sufficient shear forces within the drum to produce cavitation in the liquid dry-cleaning composition. Finally, in an alternate embodiment of the invention, agitation may be imparted by means of jet agitation as described in U.S. Patent No. 5,467,492 to Chao et al., the disclosure of which is incorporated herein by reference. As noted above, the liquid dry cleaning composition is preferably an ambient temperature composition, and the agitating step is preferably carried out at ambient temperature, without the need for associating a heating element with the cleaning apparatus.

The present invention is explained in greater detail in the following non-limiting examples.

EXAMPLES 1-2

This example shows that various CO_2 detergent formulations show a significantly enhanced cleaning effect over a commercial perchloroethylene ("perc") dry cleaning system. Small (2" x 2") swatches of various delicate (often "dry clean only") cloth were uniformly stained and run in both perc and CO_2 cleaning systems. Two CO_2 cleaning systems were employed, as follows:

FIRST:

0.5% X-207 (a commercial detergent from Union Carbide—di-nonyl phenyl ethoxylate with a hydrophobic-lipophilic balance (HLB) of about 10.5);

0.5% PDMS-g_3-PEG (polydimethyl siloxane-graft-polyethylene glycol copolymer) (500 g/mol PDMS with 350 g/mol peg grafts ca. 50 wt% PEG);

1% Span™ 80 (a commercial sorbitan ester surfactant from ICI);

0.5% isopropanol;

0.2% water;

30% Isopar™ M (a commercial hydrocarbon solvent manufactured by EXXON); and

CO_2 to balance; or

SECOND:

1% X-207;

1% Span™ 80;

1% isopropanol;

0.2% water;

30% Isopar™ M; and

CO_2 to balance.

The second system above is currently preferred.

At a temperature of 22°C to 27°C, the formulation and cloth was added to the test vessel. The test vessel was presurized with liquid CO_2 to 800-900 psi, with the total liquid volume equal to about half the vessel volume. The cloth was washed with agitation for ten minutes. To rinse, the liquid CO_2 was vented, the cloth spun for five minutes, liquid CO_2 was again added and pressurized to 800 to 900 psi until the vessel was one half full, and the cloth again agitated for five minutes. The rinse cycle (vent, spin, agitate) was repeated, the system vented and the cloth removed.

Control "perc" samples were run in perchloroethylene using a standard loading of Fabritech™ detergent and sizing, at a local commrcial dry cleaner under normal operating conditions. In each case the stained samples of cloth were washed in one of the CO_2 mixtures described above, followed by extraction and rinse with clean CO_2.

The following cloth samples were run:

1. White linen suiting
2. Acetate taffeta
3. Silk twill
4. 100% wool flannel
5. Bright filament viscose twill
6. Texturized nylon 6,6 stretch fabric
7. Texturized stretch Dacron™

Results are given in **Table 1** below. These data show that CO_2-based dry cleaning formulations of the present invention have an enhanced cleaning effect as compared to a commercial PERC dry cleaning system.

TABLE 1.

Cloth	Stain	PERC result	CO2 result
2, 4, 1	French salad dressing	slight residue remaining	visually clean, no residue
1, 2, 3, 4, 6	Spaghetti sauce	majority of stain remaining	slight residue remaining
5	Tea	over ½ of residue remaining, plus darkening of 'ring' around the stained area	slight residue remaining, no 'ring' apparent
2	Tea	slight residue remaining	visually clean, no residue
5	Blackberry juice	slight residue remaining	visually clean, no residue
4, 5, 7	Grass	slight residue remaining	minute residue remaining[1]
4	Coke™ cola beverage	½ of stain remaining	minute residue remaining
4	Coffee	½ of stain remaining	minute residue remaining
1	Egg	no significant removal of stain, slight color change of stain	slight residue remaining
1, 2, 4, 6	taco sauce	majority of stain remaining	slight residue remaining

[1]By "minute" is meant significantly less than the perc result.

EXAMPLE 3

An additional liquid carbon dioxide cleaning system, or wash fluid, that can be used in the methods described herein, is a mixture that contains:

2.86% ISOPAR M™ organic solvent;

1.23% DPMA (dipropyleneglycol menomethyl ether acetate);

0.56% TERGITOL 15-S-3™ (Union Carbide secondary alcohol ethoxylate with an HLB of 8.3);

0.28% water;

0.05% TRITON GR-7M™ (commercial detergent from Union Carbide--sodium dioctylsulfosuccinate in petroleum distillates);

0.02% TRITON RW-20™ (commercial detergent from Union Carbide--ethoxylated alkylamines); and

liquid carbon dioxide to balance.

EXAMPLE 4

An additional example of a liquid dry cleaning system useful for carrying out the present invention is a a mixture that contains:

2.80% DPM (dipropyleneglycol monomethyl ether);

1.20% hexylene glycol;

0.50% TERGITOL 15-S-3™ detergent;

0.50% water; and

liquid carbon dioxide to balance.

EXAMPLE 5

An additional example of a liquid dry cleaning system useful for carrying out the present invention is a mixture that contains:

2.80% DPM;

1.20% hexylene glycol;

0.50% TERGITOL 15-S-3™ detergent;

0.40% water;

0.10% C-300™ (commercial detergent formulation from ADCO containing quaternary amines and optical brighteners); and

carbon dioxide to balance.

EXAMPLE 6

An additional example of a liquid dry cleaning system useful for carrying out the present invention is a mixture that contains:

2.80% ISOPAR M™ organic solvent;

1.20% DPMA;

0.50% water;

0.35% EMCOL 4500™ (a commercial detergent from Witco—70% dioctyl sodium sulfonate, 30% ethanol, 10% water)

0.15% ACTRAFOS 110™ (Commercial detergent from Actrachem—phosphate ester of complex aliphatic hydroxyl compound); and

liquid carbon dioxide to balance.

EXAMPLE 7

An additional example of a liquid carbon dioxide dry cleaning system that can be used to carry out the present invention is a mixture that contains:

2.80% TPM (tripropyleneglycol monomethyl ether);

1.20% propylene carbonate;

0.50% PLURONIC L31™ (commercial detergent from BASF—polyethylene oxide-polypropylene oxide block copolymer);

0.40% water;

0.10% lauryl sulfobetaine; and

liquid carbon dioxide to balance.

EXAMPLE 8

An additional example of a liquid carbon dioxide dry cleaning system that can be used to carry out the present invention is a mixture that contains:

2.80% ISOPAR M™ organic solvent;

1.20% DPMA;

0.60% PLURONIC L31™ detergent;

0.60% water;

0.10% cyclohexanol; and

liquid carbon dioxide to balance.

EXAMPLE 9

An additional example of a liquid carbon dioxide dry cleaning system that can be used to carry out the present invention is a mixture that contains:

4.0% ISOPAR M™ organic solvent;

0.7% sodium dioctylsulfosuccinate;

0.3% water; and

liquid carbon dioxide to balance.

EXAMPLE 10

An additional example of a liquid carbon dioxide dry cleaning system that can be used to carry out the present invention is a mixture that contains:

4.00% ISOPAR M™ organic solvent;

0.62% WITCONATE P1059™ (commercial detergent of Witco—isopropylamine salt of dodecylbenzene sulfonate);

0.35% water;

0.03% TRIS™ pH buffer (tris[hydroxymethyl]aminomethane); and

liquid carbon dioxide to balance.

EXAMPLE 11

An additional example of a liquid carbon dioxide dry cleaning system that can be used to carry out the present invention is a mixture that contains:

4.2% ISOPAR M™ organic solvent;

0.24% water;

0.196% TRITON™ RW-20 (commercial detergent available from Union Carbide; a secondary amine ethoxylate);

0.048% TRITON™ GR-7M detergent (a commercial detergent of Union Carbide; sodium dioctyl sulfosuccinate in aromatic and aliphatic hydrocarbons)

0.48% TERGITOL™ 15-S-3 detergent (a commercial detergent of Union Carbide; a secondary alcohol ethoxylate); and

liquid carbon dioxide to balance.

EXAMPLE 12

An additional example of a liquid carbon dioxide dry cleaning system that can be used to carry out the present invention is a mixture that contains:

3.07% ISOPAR M™ organic solvent;

1.32% DPMA (diopropylene glycol monomethyl ether acetate);

0.087% water;

0.023% TRITON™ GR-7M detergent (a commercial detergent of Union Carbide; sodium dioctyl sulfosuccinate in aromatic and aliphatic hydrocarbons)

0.5% TERGITOL™ 15-S-3 detergent (a commercial detergent of Union Carbide; a secondary alcohol ethoxylate); and

liquid carbon dioxide to balance.

The liquid dry cleaning systems of Examples 11 and 12 are currently preferred.

The foregoing is illustrative of the present invention, and is not to be construed as limiting thereof. The invention is defined by the following claims, with equivalents of the claims to be included therein.

That which is claimed is:

1. A method for dry-cleaning garments or fabrics in carbon dioxide, comprising:

contacting a garment or fabric article to be cleaned with a liquid dry cleaning composition for a time sufficient to clean the article, said liquid dry-cleaning composition comprising a mixture of carbon dioxide, water, surfactant, and an organic co-solvent;

wherein said surfactant does not contain a CO_2-philic group; and then

separating the article from the liquid dry cleaning composition.

2. A method according to claim 1, wherein said liquid dry cleaning composition is at a temperature of 0° C to 30° C.

3. A method according to claim 1, wherein said organic co-solvent has a flash point above 140°F.

4. A method according to claim 1, wherein said organic co-solvent has a flash point above 170°F.

5. A method according to claim 1, wherein said organic co-solvent has a flash point above 200°F.

6. A method according to claim 1, wherein said organic co-solvent is a hydrocarbon co-solvent.

7. A method according to claim 1, wherein said organic co-solvent is an alkane co-solvent.

8. A method according to claim 7, said liquid dry cleaning composition further comprising an alcohol.

9. A method according to claim 1, wherein said contacting step is carried out by jet agitation.

10. A method for dry-cleaning garments or fabrics in carbon dioxide, comprising:

(a) combining a garment or fabric article to be cleaned and a liquid dry cleaning composition in a closed drum so that said closed drum contains both a liquid phase and a vapor phase, said liquid dry cleaning composition comprising a mixture of liquid carbon dioxide, water, surfactant, and a hydrocarbon co-solvent;

(b) agitating said article in said drum so that said article contacts both said liquid dry cleaning composition and said vapor phase for a time sufficient to clean said article; and then

(c) removing the cleaned article from said drum.

11. A method according to claim 10, wherein said drum is a horizontal rotating drum, and said agitating step is carried out by rotating said drum.

12. A method according to claim 10, wherein said drum is a vertical drum having an agitator positioned therein, and said agitating step is carried out by moving said agitator.

13. A method according to claim 10, wherein said liquid dry cleaning composition is a room-temperature composition and said agitating step is carried out at a temperature of 0° C to 30° C.

14. A method according to claim 10, wherein said surfactant contains a CO_2-philic group.

15. A method according to claim 10, wherein said surfactant does not contain a CO_2-philic group.

16. A method according to claim 10, wherein said organic co-solvent has a flash point above 140°F.

17. A method according to claim 10, wherein said organic co-solvent has a flash point above 170°F.

18. A method according to claim 10, wherein said organic co-solvent has a flash point above 200°F.

19. A method according to claim 10, wherein said organic co-solvent is an alkane co-solvent.

20. A method according to claim 10, said liquid dry cleaning composition further comprising an alcohol.

21. A liquid dry-cleaning composition, useful for carrying out dry cleaning in carbon dioxide at or about room temperature and vapor pressure, said composition comprising:

(a) from 0.1 to 10 percent water;

(b) carbon dioxide;

(c) from 0.1 to 10 percent surfactant; and

(d) from .01 to 50 percent of an organic co-solvent;

wherein said surfactant does not contain a CO_2-philic group.

22. A liquid dry-cleaning composition according to claim 21, said composition comprising:

(a) from 0.1 to 4 percent water;

(b) carbon dioxide;

(c) from 0.5 to 5 percent surfactant; and

(d) from 4 to 30 percent of an organic co-solvent.

23. A composition according to claim 21, wherein said organic co-solvent has a flash point above 140°F.

24. A composition according to claim 21, wherein said organic co-solvent has a flash point above 170°F.

25. A composition according to claim 21, wherein said organic co-solvent has a flash point above 200°F.

26. A composition according to claim 21, wherein said organic co-solvent is a hydrocarbon co-solvent.

27. A composition according to claim 21, wherein said organic co-solvent is an alkane co-solvent.

28. A composition according to claim 21, further comprising an alcohol.

INTERNATIONAL SEARCH REPORT

Int. ional Application No
PCT/US 98/17730

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D06L1/00 C11D1/00 D06L1/02 D06L1/04 D06L1/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D06L D06F C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 16264 A (UNIV NORTH CAROLINA) 9 May 1997 see page 12, line 32 - line 36; claims 1,8,15,16,18; example 50 ---	10-14, 16-20
X	DE 39 04 514 A (OEFFENTLICHE PRUEFSTELLE UND TEXTILINSTITUT FUER VERTRAGFORSCHUNG) 23 August 1990 cited in the application see page 3, line 51 - page 4, line 1	1,2,10, 11,13,15
A	see page 4, line 19 - line 26; claims 1,2; example 2 ---	3-8
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[X] Further documents are listed in the continuation of box C. [X] Patent family members are listed in annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 November 1998	10/12/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Saunders, T

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INTERNATIONAL SEARCH REPORT

Int. ional Application No
PCT/US 98/17730

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	see page 36, line 26 - page 37, line 35; claims 1,5; example 5 & US 5 683 473 A cited in the application & US 5 683 977 A cited in the application	1,2,9
Y	EP 0 518 653 A (CLOROX CO) 16 December 1992 see page 3, line 40 - page 4, line 1; claims 1,2,4; table I	1-28
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A	see column 4, line 34 - line 46 see column 7, line 43 - column 8, line 35; claims 1,7,10 & US 5 467 492 A cited in the application	21,22
A	WO 94 01613 A (CLOROX CO) 20 January 1994 see page 7, line 6 - page 8, line 2 see page 10, line 13 - line 23; claim 1	1-8, 10-13, 16-28
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A	DATABASE TEXTILE INSTITUTE OF TEXTILE TECHNOLOGY, CHARLOTTESVILLE, VA, US SOUTHERN TEXTILE NEWS (VOL.53, NO.. 33:12), 25 August 1997 "NCSU COLLEGE OF TEXTILES' RESEARCHER DEVELOPS ENVIRONMENTALLY SOUND CO2 DRY CLEANING" XP002085400 see abstract	1,10,14, 15,21,22
A	DESIMONE, JOSEPH M ; CANELAS, DORIAN A: "DESIGN AND UTILIZATION OF SURFACTANTS FOR CO2" 213TH ACS NATIONAL MEETING, 13 - 17 April 1997, XP002085399 SAN FRANCISCO, CA see abstract	1,10,14, 15,21,22

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